TREATMENT OF PALM OIL MILL EFFLUENT VIA CHITOSAN BASED ON FLOCCULATION
A STUDY OF DIFFERENT CONCENTRATION OF SOLID AND LIQUID CHITOSAN

SITI HAJAR BT MUSTAPA

A thesis submitted in fulfillment of the
requirements for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
University Malaysia Pahang

MAY 2008

I declare that this thesis entitled "Treatment of palm oil mill effluent via Chitosan based on flocculation: A study of different concentration of solid and liquid Chitosan" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature	: ………………………………..
Name	: SITI HAJAR BT MUSTAPA
Date	: 16 MAY 2008

DEDICATION

Special dedication to my beloved father, mother,

brothers and sisters…

ACKNOWLEDGEMENT

Assalamualaikum wbkt,

A very grateful to the Almighty, for give me strength and guidance to finish my final year project.

In preparing this thesis, I was in contact with many people. They have contributed towards my understanding and thoughts. In particular, I wish to express my sincere appreciation to my supervisor, Mr. Zulkifly bin Jemaat, whose depth of experience, has stimulated ideas in organizing my project and writing this thesis. To our final year project coordinator, Ms. Sumaiya bt Zainal Abidin, for her support and encouragement. And a special thanks to Mrs. Suhana binti Alias, for all the help rendered. I am also indebted to FKKSA lectures for their guidance to complete this thesis. Without their continued support and interest, this thesis would not have been the same as presented here.

My sincere appreciation also extends to all my colleagues and other who have provided assistance at various occasions. Their views and tips are useful indeed. Unfortunately, it is not possible to list all of them in this limited space. I am grateful to all my members in Universiti Malaysia Pahang.

ABSTRACT

Chitosan is a natural cationic biopolymer was used as a coagulant in treatment of residual oil and suspended solids in palm oil mill effluent (POME). POME is one of the major oily wastewater in Malaysia. Like other industries, palm oil processing industries also generate large quantities of effluent, when discharged untreated into watercourses, adversely affects aquatic life and domestic water supply. The objective of this study is to treat the palm oil mill effluent (POME) using the natural polymer, Chitosan based on flocculation. POME was treated using solid and liquid Chitosan to study the effect on oil removal, turbidity and biochemical oxygen demand (BOD). A study of flocculation was carried out using a jar-test apparatus. The results obtained showed that at 6.0% of liquid dosage used for treatment has reduced 80% of residual oil and 97% of turbidity. In term of Biochemical Oxygen Demand, the results showed increasing in BOD_3 reading. The results obtained proved that Chitosan in liquid form was comparatively more efficient to solid Chitosan in removing residual oil and turbidity.

ABSTRAK

Kitosan adalah kation biopolimer semulajadi yang digunakan sebagai penggumpal untuk rawatan sisa minyak dan pepejal terampai dalam efluen industri minyak sawit (EIMS). EIMS merupakan salah satu sisa berminyak utama di Malaysia. Seperti industri lain, proses penghasilan minyak sawit menghasilkan banyak sisa buangan. Apabila disalurkan kepada anak sungai tanpa rawatan, ia boleh memberi kesan buruk kepada hidupan air dan saluran air domestik. Objektif kajian ini adalah untuk merawat EIMS dengan menggunakan polimer semulajadi iaitu Kitosan menggunakan kaedah penggumpalan. EIMS dirawat dengan pepejal dan cecair Kitosan untuk mengkaji kesan pengurangan sisa minyak, kekeruhan dan keperluan oksigen biokimia (BOD). Alatan ujikaji-jar digunakan untuk proses penggumpalan. Keputusan experiment menunjukkan, apabila dirawat dengan 6.0% cecair Kitosan sisa minyak dan kekeruhan telah berkurang kepada 80% dan 97%. Dalam konteks BOD, cecair dan pepejal Kitosan keputusan menunjukkan peningkatan bacaan BOD. Keputusan membuktikan cecair Kitosan lebih efisyen berbanding pepejal Kitosan dalam mengurangkan sisa minyak dan kekeruhan.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research overview

In the development of jungle to oil palm, in addition to socio- economic considerations, the palm oil industry has and will continue to place strong emphasis on balancing environment protection and human welfare (M.A Fuad *et al.*, 1999). POME treatment requires an efficient system in facing the current challenges. There are many processing plants failed to achieve the standard discharge limits even though they have applied biological treatment system.

Therefore, an alternative POME treatment system is required to meet standard discharge limits. A technological shift from biological and chemical treatment to coagulation–flocculation process with environmental friendly coagulants could result to the improved the POME treatment system.

In this research, natural biopolymer, Chitosan will be used to treat oil and grease in POME based on flocculation followed by sedimentation. Chitosan, poly (d-glucosamine) a natural deacetylated marine polymer has been used in a variety of practical fields including wastewater management, pharmacology, biochemistry, and biomedical (Majeti, 2000; Feng *et al*., 2000).

Chitosan chain structure has positively charged amine (NH_2) functional groups which are responsible for the polyelectrolyte behavior. Chitosan could coagulate negatively charged material with its positively charged functional group to give electric neutrality. Its largest use is still has a non-toxic flocculent in the treatment of organically polluted wastewaters (An *et al*., 2001).

Flocculation followed by sedimentation is used worldwide in the wastewater treatment process before discharge the treated water to the river. Many coagulants are widely used in the conventional wastewater treatment processes. coagulants can be inorganic coagulants (e.g., aluminium sulfate and polyaluminium chloride), synthetic organic polymers (e.g., polyacrylamide derivatives) or naturally occurring flocculants (e.g., microbial flocculants). These flocculants are used for different purposes depending on their chemical characteristics. Chitosan will be used as the flocculants in this study due to its property of novel binding of the oil and grease.

1.2 Overview of Malaysian Palm Oil Industry

The Malaysian palm oil industry has seen unprecedented growth in the last four decades to emerge as the leading agricultural industry in the country. Presently about half of the agricultural land in Malaysia is under oil palm and the area is expanding. Malaysia today is the world largest producer and exporter of palm oil. In the 1997, the country produced 9.07 million tones of crude palm oil, exporting the bulk of its products and earning the country RM12.9 billion in revenue (Gurmit *et al.*,1999).

The palm oil industry is primarily export-oriented. In 2006, palm oil, being the largest contributor to the agricultural sector, recorded strong export earnings of RM21.6 billion or 51.4% of total agricultural exports value during the year, propelled by continuous R&D efforts to boost industry output and productivity.

Besides, palm oil is a natural source of Vitamin E, the tocopherols, and tocotrienols. These components are important dietary essentials, whose main function is to act as anti-oxidants, substance that prevent oxidation. Free radicals are formed in the body during normal metabolic processes leading to the oxidant of the fatty acids component on the cell membrane. The tocopherols and tocotrienols in palm oil act as natural antioxidants, scavenging the free radicals and are hence hypothesized to play a protective role against cellular aging, atherosclerosis and cancer.

Unprocessed palm oil is used in a number of countries for cooking and is also a very rich source of beta-carotene, an important source of Vitamin A. Palm oil is physically and chemically different from either palm kernel or coconut oil and should not be considered similar to these oils. Palm oil also contains a much higher proportion of palmitic acids than other fats and oils. Palm oils is used worldwide as a cooking oil, shortening and margarine and also incorporated as a component into numerous fat blends and a wide variety of food products. Palm oil, like other vegetable oils, is cholesterol free.Like other common edible fats and oils, palm oil is easily digested, absorbed an utilized for the support of healthy growth and plays a critical role in providing nutrition worldwide.

While it is recognized that the revenue from palm oil industry has contributed much towards the national development and improvement in the standard of the living of the people, the rapid expansion of the industry has also contributed to the environment pollution (A.N. Ma, 1999). Oil palm cultivation and processing like other agricultural and industrial activities, raises environmental issues.

It is mandatory for all palm oil mills to treat their waste waters on site to an acceptable level before it is allowed to be discharged into the water courses (A.N. Ma, 1999). A new and improved palm oil mill effluent (POME) treatment technology would be required in order to meet the requirements of Department of Environment (DOE) discharge limits.

1.3 Problem statement

Palm oil processing mills generally discharge large volumes of wastewater. About 0.67 tonne of POME is generated for every tonne of fresh fruit bunch(FFB) processed. One of the main ingredients in palm oil mill effluents that cause severe problems is its residue oil. POME contains about 4000-6000mg/l of oil and grease, approximately 2000mg/l of residue oil is present in an emulsified form in the supernatant of POME. In terms of biochemical oxygen demand (BOD) which amounts to 25000mg/l, it is highly polluting. The suspended solids is about 4-5% in the POME are mainly cellulosic material from the fruits. Emulsified oil droplets are experienced spontaneous coalescence into larger flocs, thus making oil separation by gravity is difficult and time consuming process. This residual oil has to be removed to prevent interfaces with water treatment units, to avoid problems in the biological treatment stages.

Besides the oily characteristics of POME, the common method to treat POME using open digestion tank systems have particular disadvantages such as a long hydraulic retention time of 45–60 days, bad odour, difficulty in maintaining the liquor distribution to ensure smooth performance over huge areas and difficulty in collecting biogas,a mixture of about 65% methane, 35% carbon dioxide and true amout of hydrogen sulfide which can have detrimental effects on the environment.

In chemical precipitation process, the commonly used coagulants in wastewater treatments such as aluminium sulphate (Alum) and polyaluminum chloride (PAC) produce sludge that is difficult to dispose and in terms of health concern can cause Alzheimer's disease in long term effects.

The government acted responsibility in enacting the Environment Quality Act in1974 and specific regulations for palm oil mill effluent in 197. It is mandatory for all palm oil mills to treat their waste waters on site to an acceptable level before it is allowed to be discharged into water courses.The enactment of the environment regulations in 1975, a concerted and intensive research and development programmed has been initiated by both the public and private sector to find a cost- effective solutions in minimize the environmental impact of the palm oil industry.

Previous study has proved that Chitosan can works as a coagulation agent for treating suspended solids and residual oil in POME (A.L.Ahmad *et al.*, 2006), as a absorbent to adsorb excess oil from oily wastewater (A.L. Ahmad *et al.,* 2003) and as a coagulation agent in treatment colloidal particles in water treatment systems (Chihpin *et al.*, 2000). No major study was carried to compare the performance between solid and liquid Chitosan based on flocculation. In this research, POME sample will be treated with solid and liquid Chitosan and the performance was study based on comparison between rate of settling, reducing in residual oil and turbidity and also biochemical oxygen demand (BOD).

1.4 Objective

- The aim of this study is to study the effect of different concentration of solid and liquid chitosan based on flocculation.

1.5 Scope of study

To achieve the objectives of this research, there are three main research fields to be carried on;

- To treat the POME sample with different concentration of solid chitosan and liquid chitosan.
- To evaluate the content of oil and grease in the POME sample before and after the treatment.
- To evaluate the quality of the POME sample before and after the treatment: turbidity and dissolved oxygen.
- To analyze the settling rate of POME sample after the treatment with Chitosan.

CHAPTER 2

LITERATURE REVIEW

2.1 Palm Oil Mill Effluent (POME)

POME is an oily wastewater generated by the palm oil processing mills in Malaysia. Besides palm oil and palm kernel, a palm oil mill also generates large quantities of liquid waste which is commonly referred to as palm oil mill effluent (POME). About 0.67 tonne of POME is generated for every tonne of fresh fruit bunch (FFB) processed. POME is a colloidal suspension that contains 95–96% of water, 0.6–0.7% of oil and grease and 4–5% of total solids including 4–5% suspended solids originated from the mixture of sterilized condensate, separator sludge and hydrocyclone wastewater (Ma, 2000). It is a thick brownish color liquid and discharged at a temperature between 80 and 90 °C. It is fairly acidic with pH ranging from 4.0 to 5.0.

POME contains about 4000–6000 mg/l of oil and grease. The oil droplets of POME can be found in two phases. They either suspend in the supernatant or float on the upper layer of the suspension. The residue oil droplets in POME were solvent extractable. The extract of the oil droplets consists of 84 wt% neutral lipids and 16 wt% of complex lipids (6 wt% glygolipids and 10 wt% phospholipids). The neutral lipids consist of 74.7% triglycerides, 8% diglycerides, 0.5% monoglycerides and 0.8% free fatty acids. POME also distributes a high concentration of surface active compounds like phospholipids (10 wt%) and glycolipids (6 wt%) (Chow and Ho, 2000). The maximum allowable limit set by the Malaysian Department of Environment (DOE), 1999 for oil and grease level is 50 mg/l.

In terms of biochemical oxygen demand (BOD) which amounts to 25000mg/l, it is highly polluting. It is 100 times more polluting than the domestic sewage. The suspended solids on the POME are mainly cellulosic material from the fruits. POME is non-toxic as no chemical is added during the oil extraction process. When the biodegradable organics are discharged to a stream containing dissolved oxygen, microorganisms begin the metabolic processes that convert the organics along with the dissolved oxygen into new cells and oxidized waste products. The quantity of oxygen required for this conversion is the biochemical oxygen demand.

The process to extract the oil requires significantly large quantities of water for steam sterilizing the palm fruit bunches and clarifying the extracted oil. It is estimated that for 1 tonne of crude palm oil produced, 5 to 7.5 tonnes of water are required, and more than 50% of the water will end up as palm oil mill effluent (Ahmad *et al*., 2003). Thus, while enjoying a most profitable commodity, the adverse environmental impact from the palm oil industry cannot be ignored.

The oil and grease content of POME is an important consideration in the handling and treatment. Oil and grease are singled out for special attention as their poor solubility in water. Oil in wastewaters has to be removed in order to prevent interfaces in water treatment units, reduce fouling in process equipment, avoid problems in biological treatment stages and comply with water discharge requirements (Ahmad *et al*. 2006). Thus, the challenge of balancing the POME into a more environmental friendly waste requires a sound and efficient treatment and disposal approach.

2.2 Methods for treatment of POME

Presently, there are several options available for treatment of POME. The three most common and efficient systems adopted by the Malaysian palm oil mills are ponding system, open tank digester and extended aeration and the last one is closed tank digester with biogas recovery and land application. But 85% of palm oil mills on the country using ponding system. This system is reliable, stable and is capable of producing good quality of final discharge which meets the regulatory watercourses discharge standard.

Ponding system is cheap to construct but requires a large land area. Ponding system normally operated at normal rate. The common practice of treating POME is by using ponding and/or open digestion tank systems which have particular disadvantages such as a long hydraulic retention time of 45–60 days, bad odour, difficulty in maintaining the liquor distribution to ensure smooth performance over huge areas and difficulty in collecting biogas which can have detrimental effects on the environment. The size and configuration of the ponds, the processes are relatively difficult to control and monitor. Furthermore there is no mechanical mixing in the ponds.

Biological treatment of palm oil mill effluents (POME) has been widely studied. Some aerobic treatment approaches include: degradation of POME using a tropical marine yeast (*Yarrowia lipolytica*) NCIM 3589 in a lagoon, trickling filter (TF) and rotating biological contactors (RBC). Considering the highly organic character of POME, anaerobic process is the most suitable approach for its treatment. Several innovative treatment technologies have been developed and applied by palm oil mills to treat POME; conventional biological treatments of anaerobic or facultative digestion are the most commonly used Department of Environment, 1999.

However, this biological treatment system needs proper maintenance and monitoring as the processes rely solely on microorganisms to break down the pollutants. The microorganisms are very sensitive to changes in the environment and thus great care has to be taken to ensure that a conducive environment is maintained for the microorganisms in which to thrive (Ahmad *et al*., 2003). It also generates vast amount of biogas which contains methane, carbon dioxide and trace amounts of hydrogen sulfide. These gases are corrosive and odorous. In addition, the treated wastewater cannot be reused in the plant, and it is being discharged into the environment.

Several studies and research has been done by the government, private sector and also educational institute to find the most effective techniques to treat POME. POME treatment requires a sound and efficient system in facing the current challenges. There are many processing plants failed to comply with the standard discharge limits even though they have applied biological treatment system. Therefore, an advance POME treatment system is required to give a better solution in managing this waste that is economic and save to people and environment.

2.3 Natural polymer, Chitosan

Chitosan (N-acetyl-d-glucosamine) is a cellulose-like polyelectrolyte biopolymer which is derived from the deacetylation of chitin. The degree of deacetylation is defined as the ratio of the number of amino groups in Chitosan to the sum of the amino and acetyl groups. Chitin is widely distributed in marine nature, occurring in the insects, yeasts, fungi and exoskeletons of crustaceans. It is a non-toxic, linear cationic polymer with high molecular weight, charge density and readily to be soluble in acidic solution. Chitosan has the property to bind itself to a variety of organic contaminants, minerals, metals and oils.

Chitosan has been used for various applications such as; coagulation of colloidal particles, as a coagulant for suspended solids in food processing plants, peat land water treatment, rubber factory effluent treatment, as a chelator of heavy metals and flocculation of food emulsion waste and river silt. Chitosan is not a health threatening material because it is a biodegradable and biopolymeric material. Furthermore, Chitosan enhances the recycling of marine waste into value added item.

Chitosan has high proportions of amino functions that provide novel binding properties for residual oil and many heavy metals in wastewater (Feng *et al.*, 2000). Chitosan is positively charged and soluble in acidic to neutral solution with a charge density dependent on pH and the degree of deacetylation value. Chitosan is very famous in sequestering bile acids and fatty acids. Crosslinked chitosans was used to absorb triglycerides and adsorb reactive dyes.

In Malaysia palm oil industry, the study of Chitosan in liquid form as a coagulation in removal residue oil and suspended solid in POME showed this natural polymer can removed about 95% of oil and suspended solids (A.L. Ahmad *et al*, 2006). Besides, the study of Chitosan in powder form for the adsorption of oil in POME resulted in removal of 97-99% of residual oil (A.L. Ahmad *et al.*, 2003). Therefore, in this research, natural polymer, Chitosan will be used as a flocculants agent to study the flocculation of oil and grease, suspended solids and dissolved oxygen in POME in different liquid and solids phase of Chitosan.

Figure 2.1 showS Chitosan chain structure has positively charged amine (NH_2) functional groups which are responsible for the polyelectrolyte behavior.

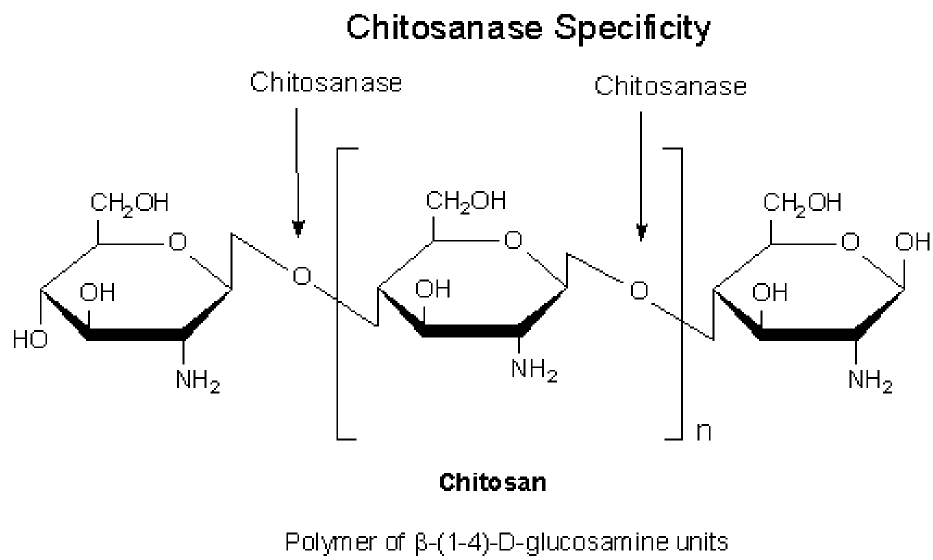

Figure 2.1: Chemical Structure for Chitosan

Chitosan could coagulate negatively charged material with its positively charged functional group to give electric neutrality. The amine functional group which attracts anionic ions to bind and bridge (Osman and Arof, 2003). This factor causes the residue oil to bind and bridge with chitosan in liquid or powder form. Therefore, chitosan a positively charged biopolymer could adsorb residue oil and destabilize the negatively charged colloids of residue oil and emulsion by charge neutralization mechanism (Jill *et al*., 1999).

Chitosan has a high charge density therefore it requires only a small amount of chitosan to destabilize the residue oil droplets.

2.4 Chitosan as a coagulation agents

Coagulant is the chemical that is dosed to cause particles to coagulate. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative charge (zeta potential) of the colloids. As a result, the particles collide to form larger particles (flocs). Rapid mixing is required to disperse the coagulant throughout the liquid.

Coagulation occurs extremely quickly. Care must be taken not to overdose the coagulants as this can cause a complete charge reversal and restabilize the colloid complex.Chitosan was used as coagulation agents in removal residual oil and suspended solids. The flocs produced by chitosan appear rapidly and grows very fast to form a larger size which can be easily sedimentated (A.L. Ahmad *et al.*, 2006).

Many coagulants are multivalent cations such as aluminium, iron, calcium or magnesium. These positively charged molecules interact with negatively charged particles and molecules to reduce the barriers to aggregation. In addition, many of these chemicals, under appropriate pH and other conditions, react with water to form insoluble hydroxides which, upon precipitating, link together to form long chains or meshes, physically trapping small particles into the larger floc.Other factors such as pH, temperature, and salinity can induce flocculation or influence flocculation rates. There are many types of natural flocculants such Chitosan , Moringa oleifera seeds, Papain , A species of Strychnos (seeds) ,and also Singlass.